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(19) (CA) **CANADIAN PATENT** (12)

(54)  $\Delta^2$ -1,2,4-Triazolin-5-One Derivatives and  
Herbicidal Compositions Containing the Same

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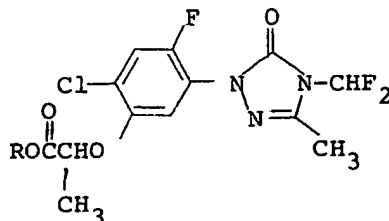
(30) PRIORITY DATE Japan (112096) 840531  
Japan (46794/85) 850309

No. OF CLAIMS 13 - NO DRAWING

Canada

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ABSTRACT OF THE DISCLOSURE

$\Delta^2$ -1,2,4-Triazolin-5-one derivatives represented by the general formula,



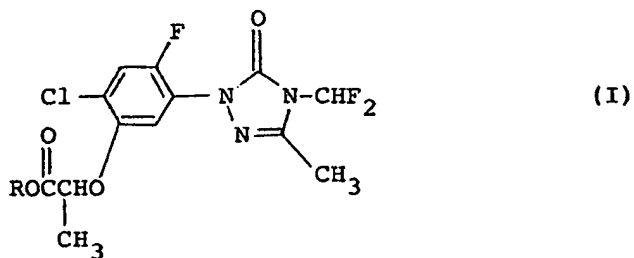
(wherein R is a hydrogen atom; an alkali metal atom; a quaternary ammonium salt; an unsubstituted-alkyl group having 1 to 6 carbon atoms; a substituted-alkyl group having halogen atoms as the substituents; an unsubstituted-cycloalkyl group; a substituted-cycloalkyl group having halogen atoms as the substituents; an alkenyl group; an alkynyl group; a lower alkoxyalkyl group; a lower alkylthioalkyl group; a lower alkylsulfinylalkyl group; a lower alkylsulfonylalkyl group; a lower alkoxyalkoxyalkyl group; a lower alkoxycarbonylalkyl group; a hydroxycarbonylalkyl group; an unsubstituted-benzyl group; a substituted-benzyl group having 1 to 2 substituents selected from the group consisting of a halogen atom, a lower alkyl group, a lower alkoxy group, a nitro group, a lower alkoxycarbonyl group, a hydroxycarbonyl group and a phenoxy group;  $\alpha$ -methylbenzyl group or a phenethyl group).

The  $\Delta^2$ -1,2,4-triazolin-5-one derivatives are useful as herbicides.

## 1 FIELD OF THE INVENTION

The present invention relates to  $\Delta^2$ -1,2,4-triazolin-5-one derivatives and herbicidal compositions containing the same as the active ingredient.

5  $\Delta^{2-1,2,4}$ -Triazolin-5-one derivatives according  
to the present invention are represented by the general  
formula (I),



(wherein R is a hydrogen atom; an alkali metal atom; a quaternary ammonium salt; an unsubstituted-alkyl group having 1 to 6 carbon atoms; a substituted-alkyl group having halogen atoms as the substituents; an unsubstituted-cycloalkyl group; a substituted-cycloalkyl group having halogen atoms as the substituents; an alkenyl group; an alkynyl group; a lower alkoxyalkyl group; a lower alkylthioalkyl group; a lower alkylsulfinylalkyl group; a lower alkylsulfonylalkyl group; a lower alkoxy-alkoxyalkyl group; a lower alkoxycarbonylalkyl group; a hydroxycarbonylalkyl group; an unsubstituted-benzyl

1 group; a substituted-benzyl group having 1 to 2 substituents  
selected from the group consisting of a halogen atom,  
a lower alkyl group, a lower alkoxy group, a nitro group,  
a lower alkoxy carbonyl group, a hydroxy carbonyl group and  
5 a phenoxy group;  $\alpha$ -methylbenzyl group or a phenethyl group).

## DESCRIPTION OF THE PRIOR ART

$\Delta^2$ -1,2,4-Triazolin-5-one derivatives represented  
by the general formula (I) according to the present  
invention are novel compounds and have not been known in  
10 any literature.

Some of similar compounds related to the above-  
mentioned  $\Delta^2$ -1,2,4-triazolin-5-one derivative represented  
by the general formula (I) are disclosed as the active  
ingredient in herbicidal compositions in Japanese Patent  
15 Kokai (Laid-open) No. Sho 57-108079 (1982) and Sho 57-  
181069 (1982).

The present inventors have found that compounds  
represented by the general formula (I) possess effective  
herbicidal activities, thus they are useful as agricultural  
20 herbicides.

Additionally, the present inventors have found  
the facts that compounds represented by the general  
formula (I) show surprisingly excellent herbicidal  
activities in relatively lower dosage and with lower  
25 phytotoxicities as compared with activities shown by  
compounds disclosed in the above-mentioned prior art  
references.

## 1 SUMMARY OF THE INVENTION

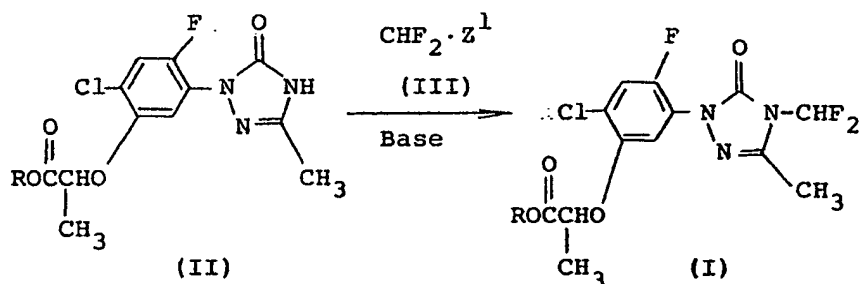
An object of the present invention is to provide novel  $\Delta^2$ -1,2,4-triazolin-5-one derivatives.

Another object of the present invention is to provide herbicidal compositions containing the  $\Delta^2$ -1,2,4-triazolin-5-one as the active ingredient.

Yet further object of the present invention is to provide processes for preparing  $\Delta^2$ -1,2,4-triazolin-5-one derivatives.

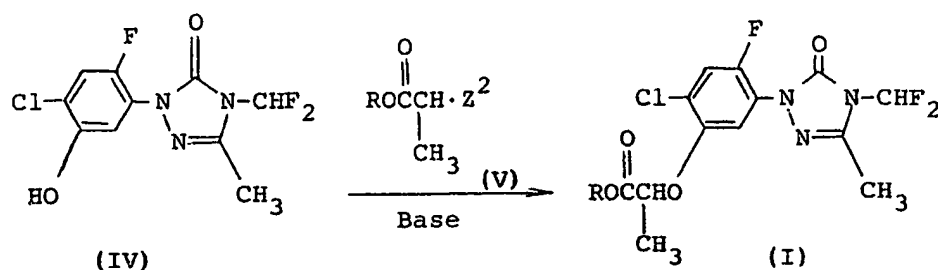
10 Compounds represented by the general formula (I) can be prepared by for example, processes method-A, method-B and method-C as follows:

## Method-A



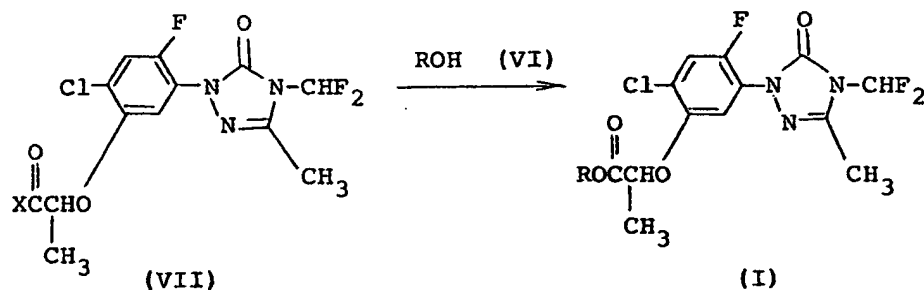
(wherein R is the same as defined above;  $\text{Z}^1$  is a chlorine atom, a bromine atom or an iodine atom).

## 1 Method-B



(wherein R is the same as defined above;  $\text{Z}^2$  is a halogen atom).

## Method-C



5 (wherein R is the same as defined above; X is a halogen atom or a hydroxyl group).

Thus, the objective  $\Delta^2$ -1,2,4-triazoline-5-one derivative represented by the general formula (I) can be prepared, in method-A, by reacting a compound represented  
 10 by the general formula (II) with a compound represented by the general formula (III); in method-B, by reacting a

1 compound represented by the general formula (IV) with a  
compound represented by the general formula (V); and in  
method-C, by reacting a compound represented by the general  
formula (VII) with a compound represented by the general  
5 formula (VI), respectively in an inert solvent, in the  
presence or absence of a basic compound.

As to the inert solvent used in these reactions,  
any inert solvent which does not give any adverse effect  
to the reactions may be employed, for example aromatic  
10 hydrocarbons such as benzene, toluene, xylene or the like  
can be exemplified; aliphatic hydrocarbons such as n-  
hexane, cyclohexane or the like can be exemplified;  
alcohols such as methanol, ethanol, propanol, ethylene  
glycol or the like can be exemplified; ketones such as  
15 acetone, methyl ethyl ketone, cyclohexanone or the like  
can be exemplified; lower aliphatic acid esters such as  
ethyl acetate or the like can be exemplified; ethers  
such as tetrahydrofuran, dioxane or the like can be  
exemplified; lower fatty acid amides such as dimethyl-  
20 formamide, dimethylacetoamide or the like can be exempli-  
fied; and water, dimethyl sulfoxide or the like can be  
exemplified. The above-mentioned solvents may be employed  
in singly or in a mixture thereof.

Further, in method-C, when an alcohol is used as  
25 the solvent, an alcohol corresponding to a compound repre-  
sented by the general formula (VI) may preferably be used.

As to the basic compound used in the above-  
mentioned reactions, inorganic basic compounds, for

1 example alkali metal hydrides such as sodium hydride or the  
like; alkali metal hydroxides such as sodium hydroxide,  
potassium hydroxide or the like; alkali metal carbonates  
such as sodium carbonate, potassium carbonate or the like;  
5 alkali metal hydrogen carbonate such as sodium hydrogen  
carbonate, potassium hydrogen carbonate or the like;  
alkali metal alcoholate such as sodium methylate or the  
like; and organic basic compounds such as pyridine, tri-  
methylamine, triethylamine, diethylaniline, 1,8-diazabi-  
10 cyclo-[5,4,0]-7-undecene or the like can be exemplified.

Reactions of the present invention can be carried  
out, for example at a temperature in the range of from 0°  
to 150°C to a predetermined temperature.

The reactions in each step therein are equimolar  
15 reactions, and in carrying out these reactions, slightly  
excess amount of one reactant to the amount of another  
reactant may be employed.

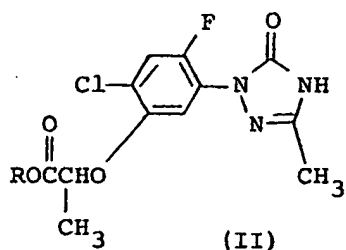
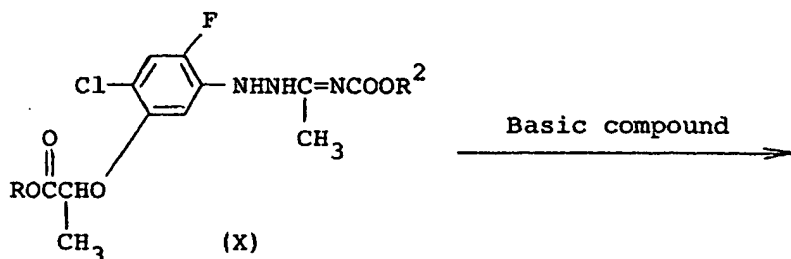
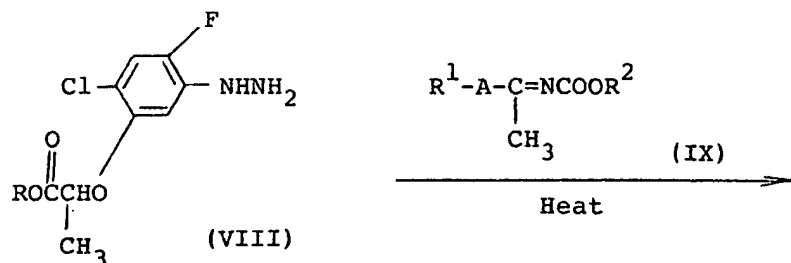
The reaction time may be selected from in the  
range of from 0.5 to 48 hours.

20 After the reaction is completed, the objective  
product can be obtained by treating the reaction product  
under a conventional manner.

Compound represented by the general formula (II)  
used as the starting material in method-A may be synthesiz-  
25 ed by the reaction steps as follows:



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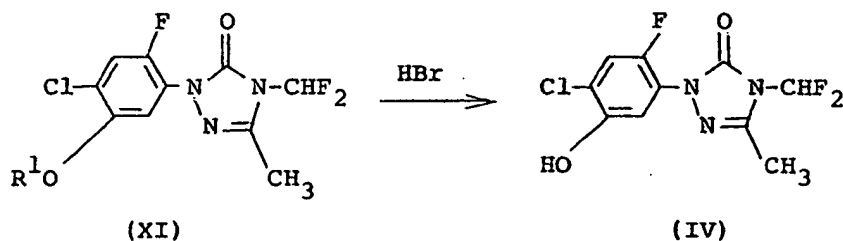


- 1 (wherein R is the same as defined above; R<sup>1</sup> and R<sup>2</sup> are each a lower alkyl group; A is an oxygen atom or a sulfur atom).

Thus, a compound represented by the general  
 5 formula (II) can be prepared by reacting a compound represented by the general formula (VIII) with a compound represented by the general formula (IX) in an inert solvent under a heating condition, then the thus obtained compound represented by the general

1 formula (X) is treated under a ring-closing reaction,  
with a basic compound, with or without being separated  
from the reaction product.

Furthermore, a compound represented by the  
5 general formula (IV) used as the starting material in  
method-B may be synthesized by the reaction step as  
follows:



(wherein R<sup>1</sup> is the same as defined above).

In the above-mentioned reaction, in place of  
10 using hydrobromic acid, there may be used hydroiodic acid  
or an alkyl thiolate.

Typical examples of Δ<sup>2</sup>-1,2,4-triazolin-5-one  
derivatives represented by the general formula (I) are shown  
in the following Table 1.

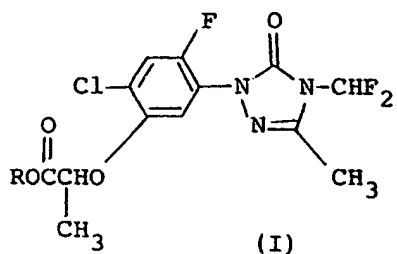




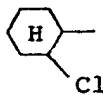
Table 1

Compound No.	R	Physical properties
1	H-	$n_D^{24.5}$ 1.5192
2	Na-	Melting point 186.1°C
3	K-	Melting point 119.2°C
4	$\oplus NH_4^-$	Melting point 92.7°C
5	<u>iso</u> -C <sub>3</sub> H <sub>7</sub> $\oplus NH_3^-$	Melting point 157.3°C
6	(C <sub>2</sub> H <sub>5</sub> ) $\oplus NH^-$	Oily substance
7	( <u>n</u> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> $\oplus NH_2^-$	Melting point 126.5°C
8	CH <sub>3</sub> -	$n_D^{23}$ 1.5142
9	C <sub>2</sub> H <sub>5</sub> -	$n_D^{10}$ 1.5112
10	<u>n</u> -C <sub>3</sub> H <sub>7</sub> -	$n_D^{23.0}$ 1.5051
11	<u>iso</u> -C <sub>3</sub> H <sub>7</sub> -	$n_D^{23.0}$ 1.5051
12	<u>n</u> -C <sub>4</sub> H <sub>9</sub> -	$n_D^{29.0}$ 1.5031
13	<u>iso</u> -C <sub>4</sub> H <sub>9</sub> -	$n_D^{29.0}$ 1.5011
14	<u>tert</u> -C <sub>4</sub> H <sub>9</sub> -	$n_D^{26.0}$ 1.5009
15	<u>n</u> -C <sub>5</sub> H <sub>11</sub> -	$n_D^{27.5}$ 1.4984
16	<u>iso</u> -C <sub>5</sub> H <sub>11</sub> -	$n_D^{26.0}$ 1.5002
17	<u>n</u> -C <sub>6</sub> H <sub>13</sub> -	$n_D^{28.5}$ 1.4992
18	ClCH <sub>2</sub> CH <sub>2</sub> -	$n_D^{26.5}$ 1.5204
19	BrCH <sub>2</sub> CH <sub>2</sub> -	$n_D^{19.5}$ 1.5291
20	Cl <sub>3</sub> CCH <sub>2</sub> -	Melting point 106.5°C
21	F <sub>3</sub> CCH <sub>2</sub> -	$n_D^{19.5}$ 1.4826
22	ClCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -	Melting point 87.7°C
23	BrCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -	Melting point 83.8°C
24	ClCH <sub>2</sub> CH-   CH <sub>3</sub>	Melting point 68.7°C

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


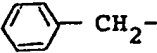
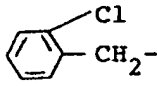
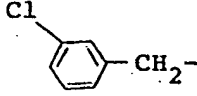
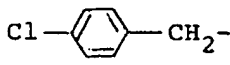
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Table 1 (Cont'd)

25	$\text{ClCH}_2\underset{\text{Cl}}{\text{CH}}\text{CH}_2^-$	Melting point 95.0°C
26	$\text{ClCH}_2\text{CH}(\text{Cl})\text{CH}_2^-$	$n_D^{14.5}$ 1.5091
27	$\text{BrCH}_2\text{CH}(\text{Br})\text{CH}_2^-$	Melting point 104.2°C
28	$\text{F}_3\text{CCH}_2\text{CH}(\text{F}_3\text{C})\text{CH}_2^-$	$n_D^{19.5}$ 1.4573
29	$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{CH}_2^-$	Melting point 95.3°C
30		$n_D^{26.0}$ 1.5130
31		$n_D^{27.5}$ 1.5140
32		$n_D^{17.5}$ 1.5174
33	$\text{CH}_2=\text{CHCH}_2^-$	$n_D^{28.5}$ 1.5156
34	$\text{CH}\equiv\text{CCH}_2^-$	$n_D^{28.5}$ 1.5192
35	$\text{CH}\equiv\text{CCH}_2\text{CH}_2^-$	$n_D^{17.5}$ 1.5209
36	$\text{CH}_3\text{O}(\text{CH}_2)_2^-$	$n_D^{26.0}$ 1.5088
37	$\text{C}_2\text{H}_5\text{O}(\text{CH}_2)_2^-$	$n_D^{26.0}$ 1.5022
38	$\text{iso-C}_3\text{H}_7\text{O}(\text{CH}_2)_2^-$	$n_D^{26.0}$ 1.4989
39	$\text{n-C}_4\text{H}_9\text{O}(\text{CH}_2)_2^-$	$n_D^{26.0}$ 1.4878
40	$\text{CH}_3\text{OCH}(\text{CH}_3)\text{CH}_2\text{CH}_2^-$	$n_D^{27.5}$ 1.5009
41	$\text{CH}_3\text{SCH}_2^-$	$n_D^{18.0}$ 1.5279
42	$\text{CH}_3\text{S}(\text{CH}_2)_2^-$	$n_D^{26.5}$ 1.5306

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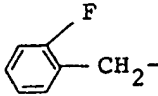
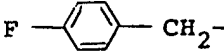
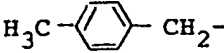

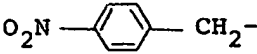
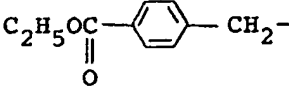
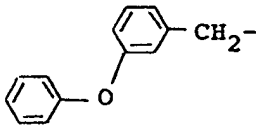
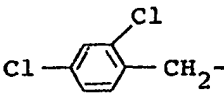
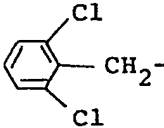
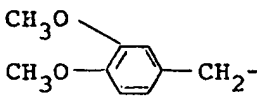
Table 1 (Cont'd)

43	$\text{C}_2\text{H}_5\text{S}(\text{CH}_2)_2^-$	$n_D^{19.5}$	1.5274
44	<u>iso</u> - $\text{C}_3\text{H}_7\text{S}(\text{CH}_2)_2^-$	$n_D^{19.5}$	1.5233
45	<u>iso</u> - $\text{C}_4\text{H}_9\text{S}(\text{CH}_2)_2^-$	$n_D^{19.5}$	1.5212
46	<u>sec</u> - $\text{C}_4\text{H}_9\text{S}(\text{CH}_2)_2^-$	$n_D^{19.5}$	1.5219
47	<u>tert</u> - $\text{C}_4\text{H}_9\text{S}(\text{CH}_2)_2^-$	$n_D^{22.5}$	1.5179
48	$\text{CH}_3\text{S}(\text{CH}_2)_3^-$	$n_D^{19.5}$	1.5299
49	$\text{C}_2\text{H}_5\text{S}(\text{CH}_2)_3^-$	$n_D^{19.5}$	1.5203
50	<u>iso</u> - $\text{C}_3\text{H}_7\text{S}(\text{CH}_2)_3^-$	$n_D^{19.5}$	1.5204
51	<u>n</u> - $\text{C}_4\text{H}_9\text{S}(\text{CH}_2)_3^-$	$n_D^{14.5}$	1.5216
52	<u>iso</u> - $\text{C}_4\text{H}_9\text{S}(\text{CH}_2)_3^-$	$n_D^{14.5}$	1.5209
53	<u>tert</u> - $\text{C}_4\text{H}_9\text{S}(\text{CH}_2)_3^-$	$n_D^{16.5}$	1.5172
54	$\text{CH}_3\text{S}(\text{CH}_2)_2^-$ 		Melting point 104.5°C
55	$\text{CH}_3\text{S}(\text{CH}_2)_2^-$ 		Melting point 99.8°C
56	$\text{CH}_3\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2^-$	$n_D^{26.0}$	1.5052
57	$\text{CH}_3\text{OC}-\text{CH}-$ 		Melting point 108.1°C
58			Melting point 82.4°C
59			Melting point 117.5°C
60			Melting point 72.6°C
61			Melting point 73.0°C

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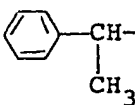
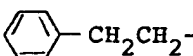
Table 1 (Cont'd)

62		Melting point 115.7°C
63		Melting point 80.0°C
64		Melting point 102.8°C
65		Melting point 89.4°C
66		Melting point 126.5°C
67		Melting point 135.3°C
68		$n_D^{26.0}$ 1.5588
69		Melting point 163.0°C
70		Melting point 114.7°C
71		Melting point 96.5°C

- Cont'd -

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Table 1 (Cont'd)

72		Oily substance
73		Oily substance

1                Next, NMR spectrum data for the compound having physical properties indicated as oily substance are shown in Table 2 below.

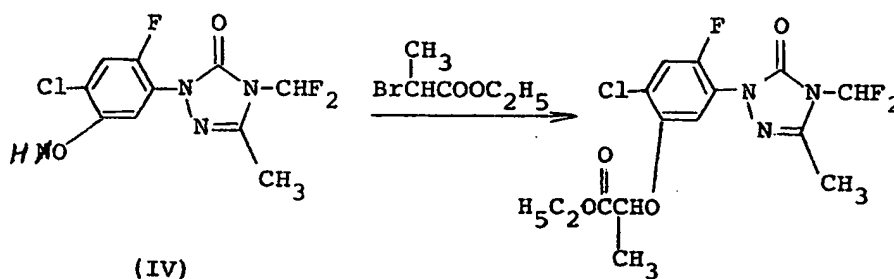
Table 2

Compound No.	NMR $\text{CCl}_4$ TMS <sup>4</sup> (ppm)
6	1.15 (t, 9H), 1.64 (d, 3H), 2.41 (s, 3H), 2.19 (q, 6H), 4.53 (q, 1H), 7.03 (t, 1H), 7.04 (d, 1H), 7.22 (d, 1H)
72	1.32-1.77 (m, 6H), 2.30 (s, 3H), 4.60 (q, 1H), 5.76 (q, 1H), 6.86 (t, 1H), 6.76-7.31 (m, 7H)
73	1.56 (d, 3H), 2.35 (s, 3H), 2.84 (t, 2H), 4.28 (t, 2H), 4.59 (q, 1H), 6.91 (t, 1H), 6.85-7.32 (m, 7H)

- 1           The present invention will be illustrated more specifically by way of showing the following examples. However, the present invention will not be restricted only to these examples.

5   Example 1

Preparation of 1-[4-chloro-2-fluoro-5-[1-(ethoxycarbonyl)ethoxy]phenyl]-4-difluoromethyl-3-methyl- $\Delta^2$ -1,2,4-triazolin-5-one (Compound No. 9)



- 13.27 Grams (0.045 mole) of compound (IV),
- 10   9.06 g (0.0498 mole) of ethyl  $\alpha$ -bromopropionate and 13.27 g (0.0962 mole) of potassium carbonate were refluxed in 200 ml of acetone with stirring for 3 hours. Then, the reaction mixture was cooled to a room temperature, and the insoluble matters were removed by filtration.
- 15   Next, the filtrate was concentrated, and the oily substance thus obtained was dissolved in diethyl ether, and washed with cold water, then the diethyl ether solution was dried, the solvent was removed by evaporation to yield an oily substance. (This oily substance was
- 20   indeed clear state as it was, and was purified by means



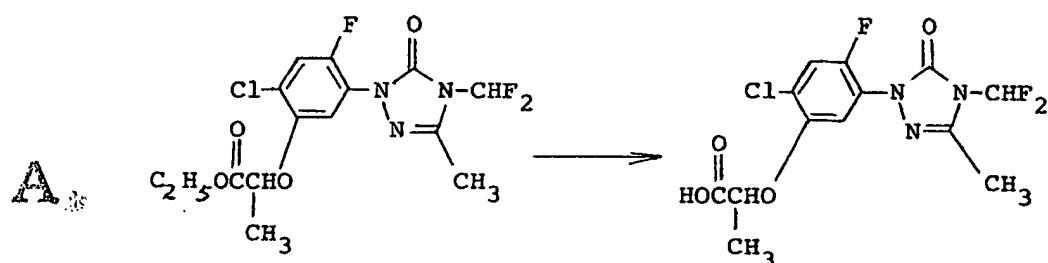
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1 of a dry column chromatography by using a silica gel.)

Yield: 14.7 g (83.1%) Refractive index  $n_D^{19.0}$  1.5112.

Example 2

Preparation of 1-{4-chloro-2-fluoro-5-[1-(hydroxycarbonyl)ethoxy]phenyl}-4-difluoromethyl-3-methyl- $\Delta^2$ -1,2,4-triazolin-5-one (Compound No. 1)

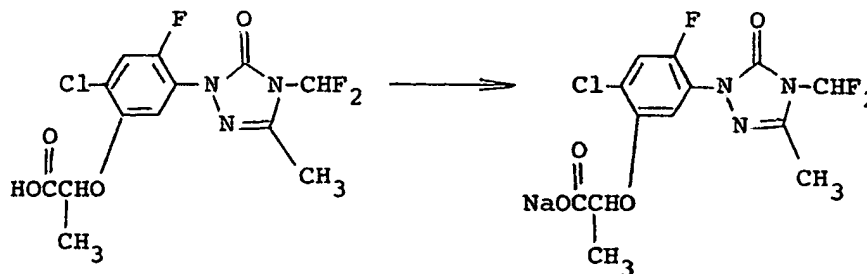


1.4 Grams (0.00356 mole) of 1-{4-chloro-2-fluoro-5-[1-(ethoxycarbonyl)ethoxy]phenyl}-4-difluoromethyl-3-methyl- $\Delta^2$ -1,2,4-triazolin-5-one was dissolved in 50 ml of ethanol, then to this solution was added 1.2 g of 20%-potassium hydroxide aqueous solution, and the whole mixture was stirred at a room temperature for 3.5 hours. After the reaction was completed, the reaction mixture was poured in an ice-water, acidified with hydrochloric acid, then the desired product was extracted with ethyl acetate. The extract was washed with water, and dried with anhydrous magnesium sulfate, then the solvent was removed by evaporation to yield 1.1 g of oily substance as the objective product.

Refractive index  $n_D^{24.5}$  1.5192. Yield 84%.

## 1 Example 3

Preparation of sodium 2-[2-chloro-5-(4-difluoromethyl-3-methyl-5-oxo- $\Delta^2$ -1,2,4-triazolin-1-yl)-4-fluorophenoxy]propionate (Compound No. 2)

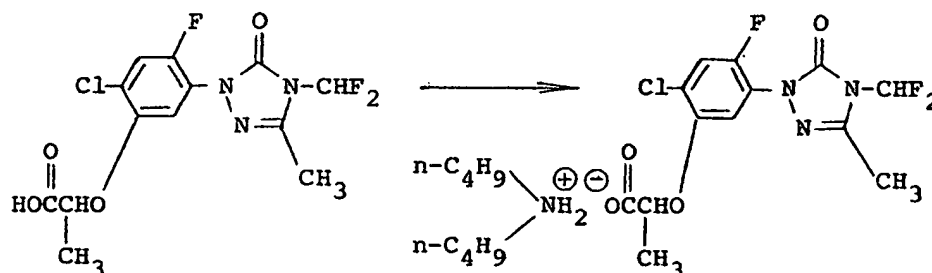


- 5 0.5 Gram (0.00136 mole) of 1-(4-chloro-2-fluoro-5-[1-(hydroxycarbonyl)ethoxy]phenyl)-4-difluoromethyl-3-methyl- $\Delta^2$ -1,2,4-triazolin-5-one was dissolved in 20 ml of tetrahydrofuran, then to this solution was added 0.05 g (0.00125 mole) of sodium hydride,
- 10 and the whole mixture was stirred at a room temperature for 10 minutes. After the reaction was completed, the tetrahydrofuran was removed by evaporation under a reduced pressure, the residue thus obtained was washed with n-hexane to yield 0.37 g of the objective product.
- 15 Melting point 186.1°C. Yield 76.4%.

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1 Example 4

Preparation of dibutylammonium 2-[2-chloro-5-(4-difluoromethyl-3-methyl-5-oxo- $\Delta^2$ -1,2,4-triazolin-1-yl)-4-fluorophenoxy]propionate (Compound No. 7)

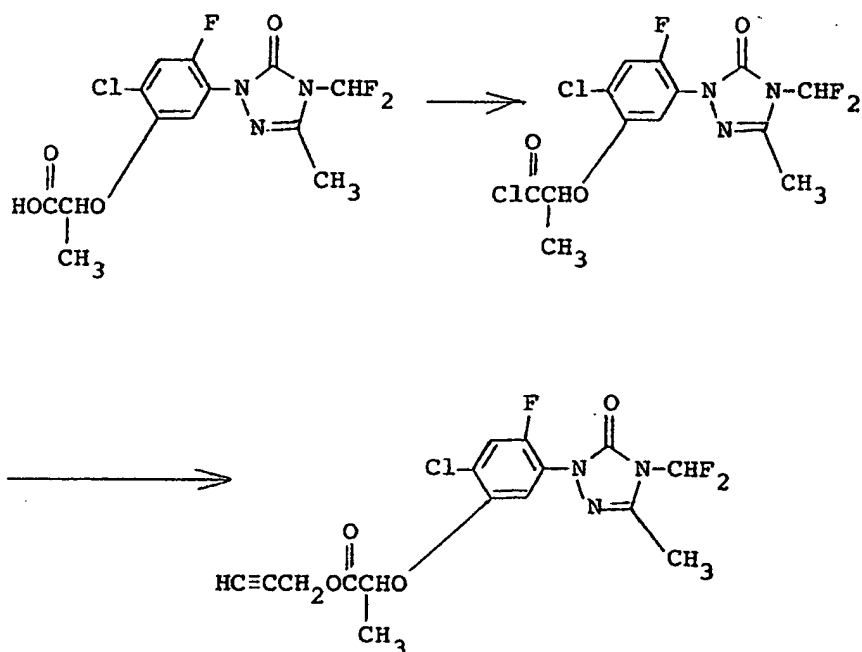


- 5                    0.5 Gram (0.00136 mole) of 1-{4-chloro-2-fluoro-5-[1-(hydroxycarbonyl)ethoxy]phenyl}-4-difluoro-methyl-3- $\Delta^2$ -1,2,4-triazolin-5-one was dissolved in 20 ml of benzene, then to solution was added 1.0 g (0.0139 mole) of dibutylamine, then under an ice-cooling condition,
- 10 the reaction was carried out. The crystals formed in the reaction mixture was collected by filtration, and washed with benzene to yield 0.51 g of the objective compound. Melting point 126.5°C. Yield 79.4%.

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1 Example 5

Preparation of 1-{4-chloro-2-fluoro-5-[1-(propargyloxycarbonyl)ethoxy]phenyl}-4-difluoromethyl-3-methyl- $\Delta^2$ -1,2,4-triazolin-5-one (Compound No. 34)



A mixed solution of 20 ml of thionyl chloride  
 5 containing 2.7 g of 1-(4-chloro-2-fluoro-5-[1-(hydroxy-  
 carbonyl)ethoxy]phenyl)-4-difluoromethyl-3-methyl- $\Delta^2$ -  
 1,2,4-triazolin-5-one was refluxed under heating for  
 2 hours. After the reaction was completed, the  
 excessive thionyl chloride was removed by evaporation,  
 10 and obtained 2.8 g of 1-(4-chloro-2-fluoro-5-[1-(chloro-  
 carbonyl)ethoxy]-phenyl)-4-difluoromethyl-3-methyl- $\Delta^2$ -  
 1,2,4-triazolin-5-one quantitatively. Then 0.5 g

1 (0.0013 mole) of this compound was dissolved in 20 ml of tetrahydrofuran, to this solution was added 0.2 g (0.00357 mole) of propargyl alcohol and 0.2 g (0.00198 mole) of triethylamine, then the whole mixture was

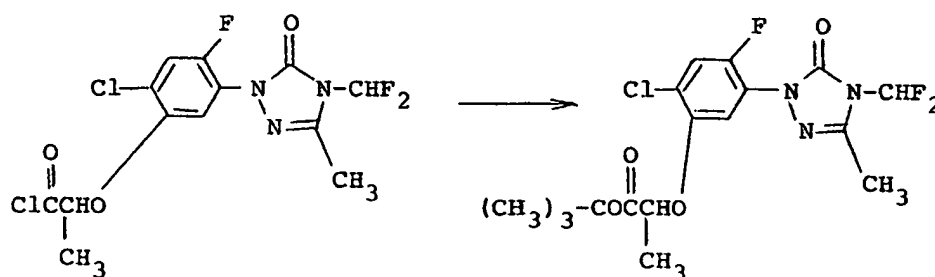
5 reacted at a room temperature for 2 hours. After the reaction was completed, the reaction mixture was poured in an ice-water, and extracted with ethyl acetate. The ethyl acetate layer was washed with an aqueous solution containing 10% of potassium carbonate, then with water,

10 dried with anhydrous magnesium sulfate, and the solvent was removed by evaporation. Thus obtained residue was purified by means of a dry column chromatography to yield 0.35 g of the objective product.

Refractive index  $n_D^{28.5}$  1.5192. Yield 66.6%.

# 15 Example 6

Preparation of 1-[5-[1-(tert-butoxycarbonyl)-ethoxy]-4-chloro-2-fluorophenyl]-4-difluoromethyl-3-methyl- $\Delta^2$ -1,2,4-triazolin-5-one (Compound No. 14)



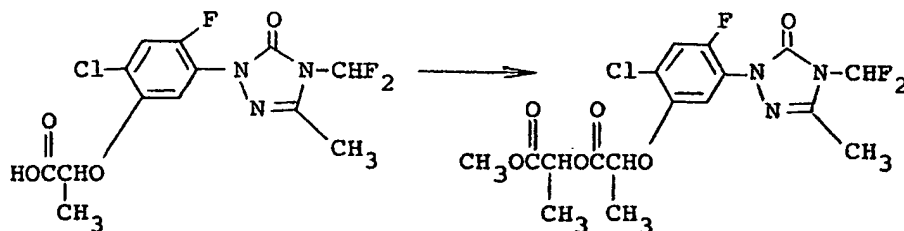
0.58 Gram (0.00151 mole) of 1-[4-chloro-2-

20 fluoro-5-[1-(chlorocarbonyl)ethoxy]phenyl]-4-difluoro-

1 methyl-3-methyl- $\Delta^2$ -1,2,4-triazolin-5-one was added in a  
 mixed solution of 0.25 g (0.00338 mole) of tert-butyl  
 alcohol, 0.14 g (60% in oil, 0.0035 mole) of sodium  
 hydride, and 20 ml of tetrahydrofuran. The whole mixture  
 5 was heated under refluxing condition for 6 hours. After  
 the reaction was completed, the reaction mixture was  
 treated under a condition similar to that described in  
 Example 5, to yield 0.13 g of the desired product.  
 Refractive index  $n_D^{26.0}$  1.5009. Yield 18.8%.

# 10 Example 7

Preparation of 1-{4-chloro-2-fluoro-5-[1-  
 [[1-(methoxycarbonyl)ethoxy]carbonyl]ethoxyphenyl]-4-  
 difluoromethyl-3-methyl- $\Delta^2$ -1,2,4-triazolin-5-one  
 (Compound No. 57)

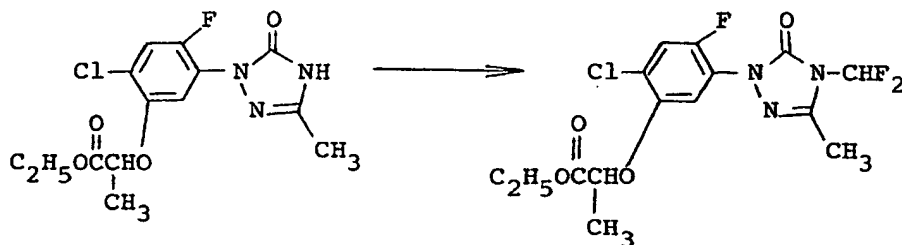


15 A mixed solution of 0.5 g (0.00136 mole) of  
 1-{4-chloro-2-fluoro-5-[1-(hydroxycarbonyl)ethoxy]phenyl}-  
 4-difluoromethyl-3-methyl- $\Delta^2$ -1,2,4-triazolin-5-one, 0.28 g  
 (0.00136 mole) of N,N'-dicyclohexylcarbodiimide, 0.02 g  
 (0.000164 mole) of 4-dimethylaminopyridine and 10 ml of  
 20 diethyl ether was reacted at a room temperature for  
 6 hours. After the completion of the reaction, the  
 insoluble matters were removed by filtration, and the

1 filtrate was treated by evaporation, the residue obtained  
 was purified by means of a dry column chromatography to  
 yield 0.41 g of the objective product. Melting point  
 108.1°C. Yield 64.3%.

5 Example 8

Preparation of 1-{4-chloro-2-fluoro-5-[1-(ethoxycarbonyl)ethoxy]phenyl}-4-difluoromethyl-3-methyl- $\Delta^2$ -1,2,4-triazolin-5-one (Compound No. 9)



0.046 Gram (0.00134 mole) of sodium hydride

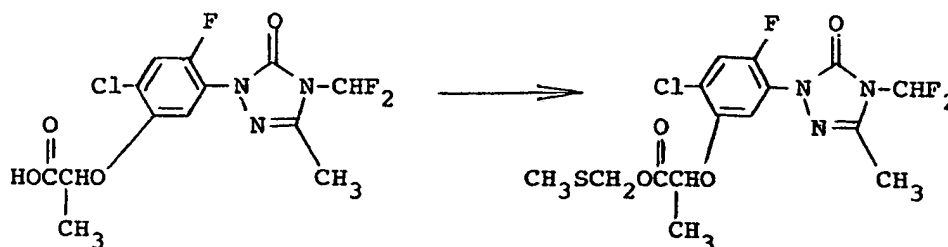
10 was suspended in 10 ml of dried N,N-dimethylformamide, to  
 this suspension was added dropwise a solution prepared by  
 dissolving 0.4 g (0.00122 mole) of 1-{4-chloro-2-fluoro-  
 5-[1-(ethoxycarbonyl)ethoxy]phenyl}-3-methyl- $\Delta^2$ -1,2,4-  
 triazolin-5-one at a room temperature. After the comple-  
 15 tion of dropwise addition, the whole mixture was stirred  
 for 30 minutes, then monochlorodifluoromethane (ClCHF<sub>2</sub>)  
 gas was introduced into the mixture at 130°C for 5 hours.  
 After the reaction was completed, the reaction mixture was  
 cooled to a room temperature, and the reaction mixture was  
 20 poured in an ice-water. The oily substance formed was  
 extracted with diethyl ether, and the extract was dried  
 with anhydrous magnesium sulfate. The solvent was removed

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1 by evaporation to yield an oily substance. This oily substance was purified by means of a dry column chromatography to yield 0.15 g of the objective product. Refractive index  $n_D^{19}$  1.5112. Yield 32.6%.

# 5 Example 9

Preparation of 1-(4-chloro-2-fluoro-5-[1-(methylthiomethoxycarbonyl)ethoxy]phenyl)-4-difluoromethyl-3-methyl- $\Delta^2$ -1,2,4-triazolin-5-one (Compound No. 41)



A mixture of 0.5 g (0.00137 mole) of 1-(4-chloro-2-fluoro-5-[1-(hydroxycarbonyl)ethoxy]phenyl)-4-difluoromethyl-3-methyl- $\Delta^2$ -1,2,4-triazolin-5-one, 1.76 g (0.00128 mole) of tert-butyl bromide, 1.15 g (0.00137 mole) of sodium hydrogen carbonate and 10 ml of dried dimethyl sulfoxide was reacted under stirring condition at a room temperature for 32 hours. After the completion of the reaction, the reaction product was treated by a method similar to that described in Example 8 to yield 0.4 g of the objective product. Refractive index  $n_D^{18.0}$  1.5279. Yield 68.7%.



1           The  $\Delta^2$ -1,2,4-triazolin-5-one derivatives of the  
 present invention are capable of controlling annual and  
 perennial weeds grown in paddy fields, upland fields,  
 orchards and swamps, for example barnyard grass (*Echino-*  
 5 *chloa crusgalli Beauv.*, an annual weed of Gramineae family  
 grown in paddy fields and strongly injurious), monochoria  
 (*Monochoria vaginalis Presl*, a strongly injurious annual  
 weed of Pontederiaceae family grown in paddy fields),  
 smallflower umbrellaplant (*Cyperus difformis L.*, an inju-  
 10 rious annual weed of Cyperaceae family grown in paddy  
 fields), slender spikerush (*Eleocharis acicularis Römer*  
*et Schultes*, a typical injurious perennial weed of  
 Cyperaceae family grown in paddy fields, and also grown  
 in swamps and waterways), arrowhead (*Sagittaria pygmaea*  
 15 *Miq.*, an injurious perennial weed of Alismataceae family,  
 grown in paddy fields, swamps and ditches), bulrush  
 (*Scirpus juncoides Roxb.* var. *Hotarui Ohwi*, an annual  
 weed of Cyperaceae family, grown in paddy fields, swamps  
 and ditches), wild oats (*Avena fatua L.*, an annual weed  
 20 of Gramineae family, grown in plains, waste lands and  
 upland fields), mugwort (*Artemisia princeps Pamp.*, a  
 perennial weed of Compositae family, grown in cultivated  
 and uncultivated fields), large crabgrass (*Digitaria*  
*adscendens Henr.*, an annual weed of Gramineae family which  
 25 is a typical strongly injurious weed grown in upland  
 fields and orchards), Gishi-gishi (*Rumex japonicus*  
*Houttuyn*, a perennial weed of Polygonaceae family, grown  
 in upland fields and on roadsides), umbrella sedge

- 1 (Cyperus iria L., an annual weed of Cyperaceae family,  
grown in upland fields and on roadsides), redroot pigweed  
(Amaranthus varidis L., an annual weed of Amaranthaceae  
family grown in upland fields, vacant lands and roadsides),  
5 and cocklebur (Xanthium Strumarium L., an annual weed of  
Compositae family, strongly injurious to soybeans).

Since,  $\Delta^2$ -1,2,4-triazolin-5-one derivatives  
represented by the general formula (I) exhibit excellent  
controlling effects against weeds of both pre- and post-  
10 emergent stages, they are useful as herbicides for soil  
treatment before and after seeding (planting), for soil  
treatment in the growth period, for foliar treatment  
before seeding (planting), for foliar treatment in the  
growth period of useful upland crops such as soybeans,  
15 cotton, corns and the like. Furthermore, these derivatives  
are useful as herbicides applying at the initial stage  
and the middle stage of rice grown in paddy fields,  
moreover, they are useful as herbicides to control general  
weeds grown in for example, ridges between paddy fields,  
20 agricultural pathways, waterways, pasture, graveyards,  
parks, roads, playgrounds, unoccupied areas around build-  
ings, reclaimed lands, railways and forests. Herbicidal  
treatments of such areas are carried out most effectively  
and economically when weeds are not emergence but not  
25 necessarily be done prior to the emergence of weeds.

For applying the derivatives of the present  
invention as herbicides, they are generally formulated,  
according to conventional procedures for preparing

1 agricultural compositions, into a form convenient to use.  
That is, derivatives of the present invention are mixed  
with suitable insert carriers and, if necessary, further  
mixed with adjuvants, in a suitable ratio, and through  
5 dissolution, dispersion, suspension, mechanical mixing,  
impregnation, adsorption or adhesion, to make the mixture  
into a suitable form of composition, e.g., suspensions,  
emulsifiable concentrates, solutions, wettable powders,  
dusts, granules or tablets.

10 As to the carriers to be used in the agricultural  
compositions may be either solid carriers or liquid  
carriers. Examples of acceptable solid carriers may be  
cited vegetable powders such as soybean flour, cereal  
flour, wood flour, bark flour, saw dust, powdered tobacco  
15 stalks, powdered walnut shell, bran, powdered cellulose,  
and extraction residues of vegetables; fibrous materials  
such as paper, corrugated paperboard, and waste cloths;  
synthetic polymers such as powdered synthetic resins;  
inorganic or mineral products such as clays (e.g., kaolin,  
20 bentonite and acid clay), talc products (e.g., talc and  
pyrophyllite), silica products [e.g., diatomaceous earth,  
silica sand, mica and white carbon (a highly dispersed  
synthetic silicic acid, also called as finely pulverized  
hydrated silica or hydrated silicic acid, and some of  
25 commercially available products contain calcium silicate  
as the major component)], activated carbon, powdered  
sulfur, pumice, calcined diatomaceous earth, ground brick,  
fly ash, sand, calcium carbonate, and calcium phosphates;

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- 1 chemical fertilizers such as ammonium sulfate, ammonium phosphates, ammonium nitrate, urea, and ammonium chloride; and farmyard manures. These solid carriers may be used alone or in combination with one another. As to the
- 5 acceptable liquid carriers are selected from those which are solvents for the active ingredients and those which are non-solvent but can disperse the active ingredients with the aid of adjuvants. Examples of these liquid carriers may be used alone or in combination with one
- 10 another, are water, alcohols (e.g., methanol, ethanol, isopropanol, butanol, and ethylene glycol), ketones (e.g., acetone, methyl ethyl ketone, methyl isobutyl ketone, diisobutyl ketone, and cyclohexanone), ethers (e.g., diethyl ether, dioxane, cellosolves, dipropyl
- 15 ether, and tetrahydrofuran), aliphatic hydrocarbons (e.g., gasoline and mineral oils), aromatic hydrocarbons (e.g., benzene, toluene, xylene, solvent naphtha, and alkyl-naphthalene), halogenated hydrocarbones (e.g., dichloroethane, chlorinated benzenes, chloroform and
- 20 carbon tetrachloride), esters (e.g., ethyl acetate, dibutyl phthalate, diisopropyl phthanate, and dioctyl phthalate), acid amides (e.g., dimethylformamide, diethylformamide, and dimethylacetamide), and nitriles (e.g., acetonitrile), and dimethyl sulfoxide.
- 25 As to the adjuvants, which are exemplified below, are used according to individual purposes. In some cases, they are used in combination with one another. In some other cases, no adjuvant is used at all.

1           For the purpose of emulsification, dispersion,  
solubilization and/or wetting of the active ingredients,  
there can be used surface active agents, for example  
polyoxyethylene alkylaryl ethers, polyoxyethylene alkyl  
5 ethers, polyoxyethylene higher fatty acid esters,  
polyoxyethylene resinates, polyoxyethylene sorbitan  
monolaurate, polyoxyethylene sorbitan monooleate, alkyl-  
arylsulfonates, naphthalenesulfonic acid condensation  
products, ligninsulfonates, and higher alcohol sulfate  
10 esters. For the purpose of stabilizing the dispersion,  
tackification and/or agglomeration of the active  
ingredients, the following materials may be used, for  
example, casein, gelatin, starch, alginic acid, methyl-  
cellulose, carboxymethylcellulose, gum arabic, polyvinyl  
15 alcohol, pine root oil, rice bran oil, bentonite and  
ligninsulfonates.

For the purpose of improving the flow property  
of the solid compositions, it is recommendable to use  
waxes, stearates, or alkyl phosphates.

20           As to peptizers for dispersible compositions,  
it is also recommendable to use naphthalenesulfonic acid  
condensation products and condensed phosphates.

It is also possible to add anti-foaming agents  
such as for example, a silicone oil.

25           The content of the active ingredients in the  
herbicidal composition may be adjusted depend on the  
applications. For the preparation of powdered or  
granulated products, it is generally 0.5 to 20% by weight

1 of the active ingredients may be used, and for the  
preparation of emulsifiable concentrates or wettable  
powder products, it is generally 0.1 to 50% by weight  
of the active ingredients may be used.

5 For destroying various weeds, inhibiting their  
growth, or protecting useful plants from the injury  
caused by these weeds, the herbicidal composition of the  
present invention is used in a weed-destroying dosage or  
a weed growth inhibiting dosage as such or after properly  
10 diluted with or suspended in water or in other suitable  
medium, to the soil or the foliage of weeds in the area  
where the emergence or growth of weeds is undesirable.

The amount of the herbicidal composition of  
the present invention to be used depends on various  
15 factors such as, for example, the purpose of application,  
the objective weeds, the emergence or growth state of  
weeds and crops, the emergence tendency of weeds, weather,  
environmental conditions, the form of herbicidal composi-  
tion, the mode of application, the type of the field to  
20 be treated, and the time of application and others.

In applying the present herbicidal composition  
alone as a selective herbicide, it is suitable to select  
the dosage of 1 to 500 g per 10 ares. On the other hand,  
in applying the present herbicidal composition in the  
25 combined use of herbicides, the optimum dosage thereof  
is often lower than that in the single use, the present  
herbicidal composition may be used in an amount lower  
than the above, when it is used in combination with

1 another type of herbicide.

Herbicidal composition of the present invention is especially valuable for the pre-emergence treatment and initial emergence stage treatment of upland fields  
 5 and for the early stage and middle stage control of weeds in paddy fields. In order to expand both range of controllable weed species and the period of time when effective applications are possible or to reduce the dosage, the herbicidal composition of the present inven-  
 10 tion can be used in combination with other herbicides, and this usage is within the scope of the present invention.

For example, herbicidal composition of the present invention can be used in combination with one  
 15 or more of the following herbicides.

Phenoxy fatty acid type herbicides: for example,  
 2,4-D: e.g., ethyl (2,4-dichlorophenoxy)-  
 acetate

MCP: e.g., ethyl (2-methyl-4-chlorophenoxy)-  
 20 acetate, sodium (2-methyl-4-chlorophenoxy)acetate, and  
 allyl 2-(2-methyl-4-chlorophenoxy)acetate

MCBP: e.g., ethyl (2-methyl-4-chlorophenoxy)-  
 butyrate

Diclofop-methyl: methyl 2-[4-(2,4-  
 25 dichlorophenoxy)phenoxy]propanoate

Diphenyl ether type herbicides: for example,

Nitrogen: 2,4-dichlorophenyl 4-nitrophenyl  
 ether

- 1                   Chlornitrofen: 2,4,6-trichlorophenyl  
4-nitrophenyl ether
- Chlomethoxynil: 2,4-dichlorophenyl  
3-methoxy-4-nitrophenyl ether
- 5                   Acifluorfen: 5-(2-chloro- $\alpha,\alpha,\alpha$ -trifluoro-p-  
tolyoxy)-2-nitrobenzoic acid and its salts
- Fluazifop-butyl: butyl ( $\pm$ )-2-[4-[[5-  
(trifluoromethyl)-2-pyridyl]oxy]phenoxy]propionate
- Triazine type herbicides: for example,
- 10                  Simazine: 2-chloro-4,6-bis(ethylamino)-s-  
triazine
- Prometryne: 2-methylthio-4,6-bis(iso-  
propylamino)-s-triazine
- Simetryne: 2-methylthio-4,6-bis(ethylamino)-
- 15 s-triazine, and
- Metribuzin: 4-amino-6-tert-butyl-3-methylthio-  
1,2,4-triazin-5(H)-one
- Carbamate type herbicides: for example,
- Molinate: s-ethyl hexahydro-1H-azepine-1-
- 20 cabothioate
- Swep: methyl N-(3,4-dichlorophenyl)carbamate
- Chloropropham: isopropyl N-(3-chlorophenyl)-  
carbamate and
- Benthiocarb: s-(4-chlorobenzyl)diethyl-
- 25 triocarbamate
- Toluidine type herbicides: for example,
- Trifluraline: ( $\alpha,\alpha,\alpha$ -trifluoro-2,6-dinitro-N,  
N-dipropyl-p-toluidine and



- 1           Pendimethaline: N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine
- Acid amide type herbicides: for example,
- Propanil: 3,4-dichloropropionanilide
- 5           Butachlor: N-(Butoxymethyl)-2-Chloro-2,6-diethylacetanilide
- Alachlor: 2-chlor--2,6-diethyl-N-(methoxymethyl)acetanilide
- Metolachlor: 2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide and
- 10           Pretilachlor: 2-chloro-2,6-diethyl-N-(2-propoxyethyl)acetanilide
- Other types of herbicides: for example,
- Duron: 3-(3,4-dichlorophenyl)-1,1-dimethylurea
- 15           Bentazon: 3-isopropyl-(H)-2,1,3-benzothiazin-4-(3H)-one 2,2-dioxide
- Pyrazolate: 4-(2,4-dichlorobenzoyl)-1,3-dimethylpyrazol-5-yl-p-toluenesulfonate
- 20           Pyrazoxyfen: 1,3-dimethyl-4-(2,4-dichlorobenzoyl)-5-phenacyloxy-pyrazol and
- MY-71: 4-(2,4-dichloro-3-methylbenzoyl)-1,3-dimethylpyrazol-5-yl-p-toluenesulfonate
- 25           The following examples illustrate the herbicidal effects, and the herbicidal compositions of the present invention. However, the present invention will not be restricted only to these examples.

1 Herbicidal test example - 1

Controlling effect on paddy field weeds of  
pre-emergence stage

Pots (1/10,000 - are) were filed with soil to  
5 simulate a paddy field, and planted with seeds of barnyard  
grass, monochoria, umbrella plant, and bulrush, and with  
tubers of arrowhead, respectively, which are all injurious  
weeds grown in paddy fields, were conditioned so as to  
be in pre-emergence stage.

10 The soil in the pot was treated with each of  
the present compounds (listed in Table 1) formulated to  
given concentration of liquid, by spraying. After 21  
days, the percent control of weed growth compared with  
that on the untreated plot was observed and the herbicidal  
15 activity was determined according to the criterion as  
shown in the following Table 2.

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Table 2

Criterion for determining herbicidal activity

<u>Degree of herbicidal activity</u>	<u>Percent control of weed growth (%)</u>
5	100
4	90 - 99
3	80 - 89
2	70 - 79
1	Less than 70

The test results were summarized in Table 3.

Table 3

Compound No.	Amount of active ingredient (g/are)	Effect of pre-emergence treatment				
		Barnyard grass	Mono- choria	Umbrella- plant	Bulrush	Arrowhead
1	30	5	5	5	5	5
	3	5	5	5	5	5
2	30	5	5	5	5	5
	3	5	5	5	5	5
8	30	5	5	5	5	5
	3	5	5	5	5	5
9	30	5	5	5	5	5
	3	5	5	5	5	5
11	30	5	5	5	5	5
	3	5	5	5	5	5
13	30	5	5	5	5	5
	3	5	5	5	5	5
17	30	5	5	5	5	5
	3	5	5	5	5	5
18	30	5	5	5	5	5
	3	5	5	5	5	5
19	30	5	5	5	5	5
	3	5	5	5	5	5

(To be continued)





Table 3 (Continued)

69	30	5	5	5	5	5
	3	5	5	5	5	5

Reference  
Compound

A	3	3	4	4	3	3
B	3	3	4	4	3	3

Reference compound A: Compound No. 1 = 1-(2,4-Dichloro-5-isopropoxyphenyl)-4-difluoromethyl-3-methyl- $\Delta^2$ -1,2,4-triazolin-5-one as disclosed in Japanese Patent Kokai No. 57-108079 (1982)

Reference compound B: Compound No. 7 = 1-(2,4-Dichloro-5-[[1-ethoxycarbonyl]ethoxy]-phenyl)-4-difluoromethyl-3-methyl- $\Delta^2$ -1,2,4-triazolin-5-one as disclosed in Japanese Patent Kokai No. 57-181069 (1982)

## 1 Herbicidal test example - 2

Controlling effect on paddy field weeds of  
post-emergence stage

- Pots (1/10,000 - are) were filled with soil  
5 to simulate a paddy field and grown with each of injurious  
weeds of the following lead age. In addition, young  
seedlings of rice plant (cultivar: "Nihonbare") of the  
2.5 lead age were transplanted to the soil on the day  
before the treatment with each of the present herbicides.  
10 After 21 days, the herbicidal effect and the degree of  
crop injury were evaluated by comparing the results with  
those on the untreated plot.

<u>Species of weed tested</u>	<u>Leaf age of the weed</u>
Barnyard grass	1
Monochoria	2 - 3
Umbrella plant	1 - 2
Bulrush	2 - 3
Arrowhead	3
Water nutgrass	1 - 2

The criterion for judging the degree of crop  
injury are as follows:

- 15 H: High (including withering)  
M: Medium  
L: Low  
N: None

The criterion for judging the herbicidal



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1 activity is in accordance with that used in herbicidal  
test example - 1. The results were summarized in Table  
4.

Table 4

Compound No.	Amount of active ingredient (g/are)	Effect of post-emergence treatment					Crop injury Rice
		Barnyard grass	Mono- choria	Umbrella- plant	Bulrush	Arrowhead	Water nutgrass
1	30	5	5	5	5	5	5
	3	5	5	5	5	4	5
2	30	5	5	5	5	5	5
	3	5	5	5	5	5	4
8	30	5	5	5	5	5	5
	3	4	5	5	5	5	4
9	30	5	5	5	5	5	5
	3	4	5	5	5	5	5
11	30	5	5	5	5	5	5
	3	4	5	5	5	5	4
13	30	5	5	5	5	5	5
	5	5	5	5	5	5	5
17	30	5	5	5	5	5	5
	3	5	5	5	5	4	4
18	30	5	5	5	5	5	5
	3	5	5	5	5	4	5
19	30	5	5	5	5	5	5
	3	5	5	5	5	5	5

(To be continued)



(To be continued)

[illegible]

Table 4 (Continued).

69	30	5	5	5	5	5	5	L
Reference compound	3	5	5	5	4	4	4	L
A	3	2	4	4	2	3	2	L
B	3	2	4	4	2	3	2	L

Reference compounds A and B are the same as mentioned in Table 3.

1 Herbicidal test example - 3

Controlling effect on upland field weeds of  
pre-emergence stage

Polyethylene vats, having 10 x 20 x 5 cm (depth)  
5 size, were filled with soil and seeded with oats, barnyard  
grass, large crabgrass, redroot pigweed, mugwort,  
Gishi-gishi, umbrella sedge and cocklebur, respectively,  
and seeds were covered with soil.

The soil was treated with each of the present  
10 herbicides formulated to a given concentration of liquid,  
by spraying. After 21 days, the herbicidal effect was  
evaluated by comparing the results with those on the  
untreated plot. The criterion for judging the herbicidal  
activity is the same as shown in test example - 1. The  
15 results were summarized in Table 5.

Table 5  
Effect of pre-emergency treatment

Compound No.	Amount of active ingredient (g/are)	Effect of pre-emergency treatment						
		Oats	Barnyard Large grass	crabgrass	Redroot pigweed	Mugwort	Gishi- gishi sedge	Umbrella Cocklebur
1	30	5	5	5	5	5	5	5
	3	4	4	5	5	5	5	5
2	30	5	5	5	5	5	5	5
	3	4	4	5	5	5	5	5
8	30	5	5	5	5	5	5	5
	3	4	4	5	5	5	5	5
9	30	5	5	5	5	5	5	5
	3	4	4	5	5	5	5	5
11	30	5	5	5	5	5	5	5
	3	4	4	5	5	5	5	5
13	30	5	5	5	5	5	5	5
	3	4	4	5	5	5	5	5
17	30	5	5	5	5	5	5	5
	3	4	4	5	5	5	5	5
18	30	5	5	5	5	5	5	5
	3	4	5	5	5	5	5	5
19	30	5	5	5	5	5	5	5
	3	4	5	5	5	5	5	5

(To be continued)





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45	30	5	5	5	5	5	5	5	5	5	5	5	5
	3	4	5	5	5	5	5	5	5	5	5	5	5
48	30	5	5	5	5	5	5	5	5	5	5	5	5
	3	3	4	5	5	5	5	5	5	5	5	5	5
49	30	5	5	5	5	5	5	5	5	5	5	5	5
	3	4	5	5	5	5	5	5	5	5	5	5	5
53	30	5	5	5	5	5	5	5	5	5	5	5	5
	3	4	4	5	5	5	5	5	5	5	5	5	5
54	30	5	5	5	5	5	5	5	5	5	5	5	5
	3	4	5	5	5	5	5	5	5	5	5	5	5
55	30	5	5	5	5	5	5	5	5	5	5	5	5
	3	3	4	5	5	5	5	5	5	5	5	5	5
56	30	5	5	5	5	5	5	5	5	5	5	5	5
	3	3	4	5	5	5	5	5	5	5	5	5	5
58	30	5	5	5	5	5	5	5	5	5	5	5	5
	3	5	5	5	5	5	5	5	5	5	5	5	5
61	30	5	5	5	5	5	5	5	5	5	5	5	5
	3	4	5	5	5	5	5	5	5	5	5	5	5
64	30	5	5	5	5	5	5	5	5	5	5	5	5
	3	4	5	5	5	5	5	5	5	5	5	5	5
65	30	5	5	5	5	5	5	5	5	5	5	5	5
	3	4	4	5	5	5	5	5	5	5	5	5	5

(To be continued)

(To be continued)

Table 5 (Continued)

69	30	5	5	5	5	5	5	5	5	5
	3	4	5	5	5	5	5	5	5	5
Reference compound										
A	3	2	3	3	5	4	3	4	4	1
B	3	1	2	3	5	4	3	4	4	2

## 1 Herbicidal test example - 4

Controlling effect on upland field weeds of  
post-emergence stage

Polyethylene vats, having 10 x 20 x 5 cm

- 5 (depth) size, were filled with soil and seeded with the  
weeds shown below and soybean seeds, respectively, and  
the seeds were covered with soil. The weeds and soybean  
were cultivated respectively to the following leaf ages  
and then treated with each of the present active compounds  
10 at a given dosage.

After 21 days, the herbicidal effect on the  
weeds and the degree of crop injury to the soybean were  
evaluated by comparing the results with those on the  
untreated plot.

<u>Species of test plant</u>	<u>Leaf age</u>
Oats	2
Large crabgrass	2
Redroot pigweed	1
Mugwort	1
Gishi-gishi	2
Umbrella sedge	1
Cocklebur	1
Soybean	First trifoliate age

- 15 The criteria for judging the herbicidal  
activity and crop injury were in accordance with those  
used in herbicidal test examples -1 and -2, respectively.  
The results were summarized in Table 5.

Table 6

Compound No.	Amount of active ingredient (g/are)	Effect of post-emergence treatment					Crop injury
		Oats	Large crabgrass	Redroot pigweed	Mugwort	Gishi-Umbrella sedge	
1	30	5	5	5	5	5	L
	3	4	4	5	5	5	L
2	30	5	5	5	5	5	L
	3	4	4	5	5	5	L
8	30	5	5	5	5	5	L
	3	4	4	5	5	5	L
9	30	5	5	5	5	5	L
	3	4	4	5	5	5	L
11	30	5	5	5	5	5	L
	3	4	4	5	5	5	L
13	30	5	5	5	5	5	L
	3	4	4	5	5	5	L
17	30	5	5	5	5	5	L
	3	4	4	5	5	5	L
18	30	5	5	5	5	5	L
	3	4	4	5	5	5	L
19	30	5	5	5	5	5	L
	3	4	4	5	5	5	L
21	30	5	5	5	5	5	L
	3	4	4	5	5	5	L

(To be continued)

[illegible]

Table 6 (Continued)

48	30	5	5	5	5	5	5	5	5	L
49	3	4	5	5	5	5	5	5	5	L
53	30	5	4	5	5	5	5	5	5	L
54	3	4	5	5	5	5	5	5	5	L
55	30	5	4	5	5	5	5	5	5	L
56	3	4	5	5	5	5	5	5	5	L
58	30	5	4	5	5	5	5	5	5	L
61	3	4	5	5	5	5	5	5	5	L
64	30	5	4	5	5	5	5	5	5	L
65	3	4	5	5	5	5	5	5	5	L
69	30	5	4	5	5	5	5	5	5	L
	3	3	5	5	5	5	5	5	5	L

(To be continued)

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Table 6 (Continued)

Reference compound	3	2	3	4	3	2	3	2	L
A	3	2	3	4	3	2	3	2	L
B	3	2	3	4	3	3	3	2	L

## 1 Example of herbicidal composition - 1

A wettable powder composition was prepared by mixing uniformly and grinding the following ingredients:

	Compound No. 3	50 Parts
5	Mixture of clay with white carbon (in which clay is contained as the major component)	45 Parts
10	Polyoxyethylene nonylphenyl ether	5 Parts

## Example of herbicidal composition - 2

A granular composition was prepared by mixing uniformly and grinding the following ingredients, kneading the mixture with a suitable amount of water,

## 15 and granulating the kneaded mixture:

	Compound No. 25	5 Parts
	Mixture of bentonite with clay	90 Parts
	Calcium ligninsulfonate	5 Parts



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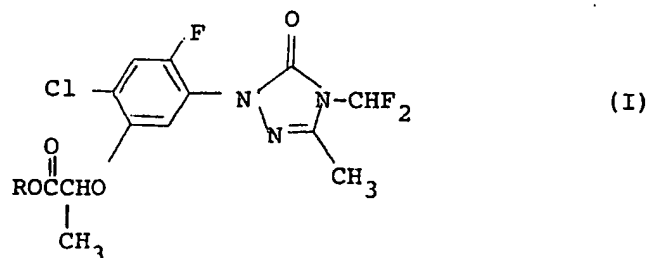
1 Example of herbicidal composition - 3

An emulsifiable concentrate was prepared by mixing uniformly the following ingredients:

	Compound No. 50	50 Parts
5	Xylene	40 Parts
	Mixture of polyoxyethylene	10 Parts
	nonylphenyl ether with	
	calcium alkylbenzenesulfonate	

WHAT IS CLAIMED IS:

1.  $\Delta^2$ -1,2,4-Triazolin-5-one derivatives represented by the general formula (I),



(wherein R is a hydrogen atom; an alkali metal atom; a quaternary ammonium salt; an unsubstituted-alkyl group having 1 to 6 carbon atoms; a substituted-alkyl group having halogen atoms as the substituents; an unsubstituted-cycloalkyl group; a substituted-cycloalkyl group having halogen atoms as the substituents; an alkenyl group; an alkynyl group; a lower alkoxyalkyl group; a lower alkylthioalkyl group; a lower alkylsulfinylalkyl group; a lower alkylsulfonylalkyl group; a lower alkoxyalkoxyalkyl group; a lower alkoxycarbonylalkyl group; a hydroxycarbonylalkyl group; an unsubstituted-benzyl group; a substituted-benzyl group having 1 to 2 substituents selected from the group consisting of a halogen atom, a lower alkyl group, a lower alkoxy group, a nitro group, a lower alkoxycarbonyl group, a hydroxycarbonyl group and a phenoxy group;  $\alpha$ -methylbenzyl group or a phenethyl group).

2. The  $\Delta^2$ -1,2,4-triazolin-5-one derivatives according to Claim 1, wherein R is a hydrogen atom; an

alkali metal atom; a quaternary ammonium salt; a substituted-alkyl group having halogen atoms as the substituents; an unsubstituted-cycloalkyl group; a substituted-cycloalkyl group having halogen atoms as the substituents; an alkenyl group; an alkynyl group; a lower alkoxyalkyl group; a lower alkylthioalkyl group; a lower alkylsulfinylalkyl group; a lower alkylsulfonylalkyl group; a lower alkoxyalkoxyalkyl group; a lower alkoxycarbonylalkyl group; a hydroxycarbonylalkyl group; an unsubstituted-benzyl group; a substituted-benzyl group having 1 to 2 substituents selected from the group consisting of a halogen atom, a lower alkyl group, a lower alkoxy group, a nitro group, a lower alkoxycarbonyl group, a hydroxycarbonyl group and a phenoxy group;  $\alpha$ -methylbenzyl group or a phenethyl group.

3. A herbicidal composition containing  $\Delta^2$ -1,2,4-triazolin-5-one derivatives as claimed in Claim 1 is contained as the active ingredient with suitable carriers.

4. The herbicidal composition according to Claim 3, wherein the active ingredient is  $\Delta^2$ -1,2,4-triazolin-5-one derivative as claimed in Claim 2.

5. 1-{4-Chloro-2-fluoro-5-[1-(2-chloroethoxycarbonyl)ethoxy]phenyl}-4-difluoromethyl-3-methyl- $\Delta^2$ -1,2,4-triazolin-5-one.
6. 1-{4-Chloro-2-fluoro-5-[1-(2-bromoethoxycarbonyl)ethoxy]phenyl}-4-difluoromethyl-3-methyl- $\Delta^2$ -1,2,4-triazolin-5-one.
7. 1-{4-Chloro-2-fluoro-5-[1-(2,2,2-trifluoroethoxycarbonyl)ethoxy]phenyl}-4-difluoromethyl-3-methyl- $\Delta^2$ -1,2,4-triazolin-5-one.
8. 1-{4-Chloro-2-fluoro-5-[1-(3-chloropropoxycarbonyl)ethoxy]phenyl}-4-difluoromethyl-3-methyl- $\Delta^2$ -1,2,4-triazolin-5-one.
9. 1-{4-Chloro-2-fluoro-5-[1-(methoxyethoxycarbonyl)ethoxy]phenyl}-4-difluoromethyl-3-methyl- $\Delta^2$ -1,2,4-triazolin-5-one.
10. 1-{4-Chloro-2-fluoro-5-[1-(isopropoxyethoxycarbonyl)ethoxy]phenyl}-4-difluoromethyl-3-methyl- $\Delta^2$ -1,2,4-triazolin-5-one.
11. 1-{4-Chloro-2-fluoro-5-[1-(methoxyethoxyethoxycarbonyl)ethoxy]phenyl}-4-difluoromethyl-3-methyl- $\Delta^2$ -1,2,4-triazolin-5-one.
12. 1-{4-Chloro-2-fluoro-5-[1-(4-chlorobenzoyloxycarbonyl)ethoxy]phenyl}-4-difluoromethyl-3-methyl- $\Delta^2$ -1,2,4-triazolin-5-one.
13. 1-{4-Chloro-2-fluoro-5-[1-(4-methylbenzyloxycarbonyl)ethoxy]phenyl}-4-difluoromethyl-3-methyl- $\Delta^2$ -1,2,4-triazolin-5-one.

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